discuss the far-infrared field-free rotational spectrum. Both types of study related to both fine-structure states, so that a more accurate separation of the individual magnetic hyperfine constants was obtained. Brown and Radford [37] were able to determine the rotational g-factors, and to use earlier field-free microwave studies to interpret the hyperfine spectrum, including the nitrogen electric quadrupole interaction for $^{14}N^{16}O$.

9.4.3. OH in the $X\,^2\Pi$ ground state

We now turn to radicals with $^2\Pi_{3/2}$ ground states which do not conform to the simple case (a) model described above. Foremost among these are OH and CH, both of which occupy extremely important places in chemistry, molecular physics, and astrophysics. OH, in particular, is probably the free radical that has been most extensively studied by high-resolution spectroscopy; the story is complex, but ultimately very well understood. OH was the first gas-phase free radical to be detected by conventional microwave rotational spectroscopy, and we described its electric resonance Λ-doubling spectrum in detail in chapter 8. It has also been investigated by both microwave and far-infrared laser magnetic resonance, as we shall describe in due course. Following that we will describe pioneering laser magnetic resonance experiments on the CH radical.

(a) Microwave magnetic resonance

(i) INTRODUCTION

The ratio B_0/A_0 for the OH radical in its ground $^2\Pi$ state is -0.1333, large compared with, for example, the ratio for ClO which is -0.0022. Consequently its coupling scheme shows a considerable departure from the Hund's case (a) limit towards case (b), particularly as J increases. Its rotational energy levels are more complicated than those of ClO and are best described as showing intermediate coupling behaviour. It is still possible to think of the pattern as two sets of rotational levels, one associated with the lower spin component and the other with the upper. However, for OH these two sets of levels are not well separated from each other but are extensively intermingled, as shown in figure 9.13. We shall see that terms in the rotational kinetic energy operator mix levels with the same J in the two spin components quite heavily. As a result, the quantum number Ω which we have used so far to label the spin components ceases to be a good one. In this situation, the lower level for a given J is referred to as the F_1 spin component and the upper one as F_2. For OH, with a negative spin–orbit coupling constant ($A_0 = -139$ cm^{-1}), the F_1 component correlates with $^2\Pi_{3/2}$ in the case (a) limit and the F_2 component with $^2\Pi_{1/2}$. This correlation is quite reliable at low J but becomes increasingly less so as J increases. We note a curiosity that, although there are always two spin components for levels with J greater than or equal to $3/2$, for $J = 1/2$ there is only one spin component which always has pure $\Omega = 1/2$ character. Nearer the case (b) limit, there can be some uncertainty whether to associate the $J = 1/2$

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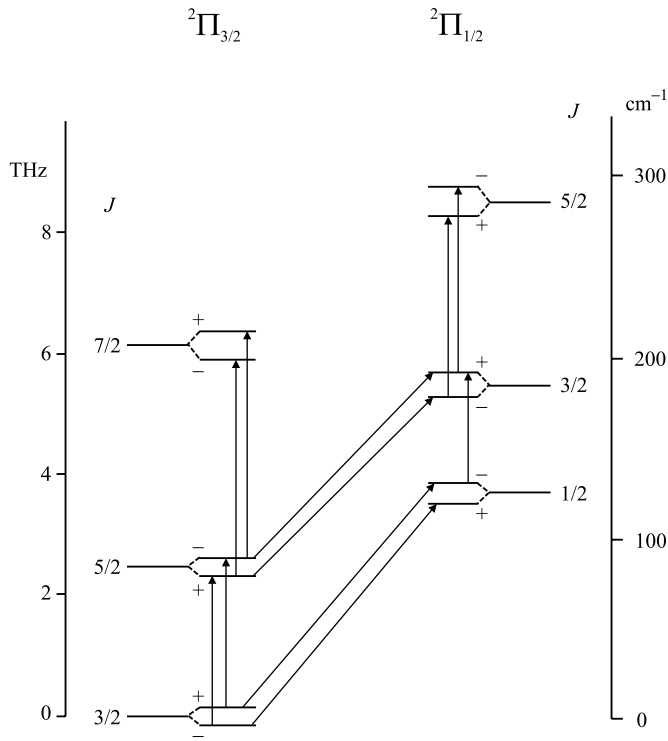

Figure 9.13. Lowest rotational levels of the OH radical and the far-infrared transitions observed. The Λ-doublet splittings are exaggerated for the sake of clarity.

level with the F_1 set or the F_2 set. Fortunately, in the case of OH, the situation is quite clear. The $J = 1/2$ level is associated with the upper set of levels and it is appropriate to label it as F_2. In addition to showing intermediate coupling behaviour, OH has a very small moment of inertia and hence a large rotational constant. As a result, its energy levels show two additional effects compared with ClO, centrifugal distortion and Λ-type doubling; we discussed the latter extensively in chapter 8 when describing the molecular beam electric resonance spectrum.

(ii) EXPERIMENTAL STUDIES

The OH radical has been studied extensively by both microwave and far-infrared laser magnetic resonance. In the microwave region, the pioneering work of Radford [7] effectively launched the field of gas phase electron resonance, which in this book we are calling microwave magnetic resonance. Radford first studied OH in the $J = 3/2$, $5/2$ and $7/2$ levels of the $^2\Pi_{3/2}$ component, and also OD in the $J = 3/2$ level. Figure 9.14 shows the behaviour of the $J = 3/2$ Λ-doublet and hyperfine levels in a magnetic field, together with the magnetic resonance electric dipole transitions. We also show a stick diagram of the observed spectrum. Radford did not show an experimental recording of any of his OH F_1 ($^2\Pi_{3/2}$) spectra, but to compensate we show, in figure 9.15, the

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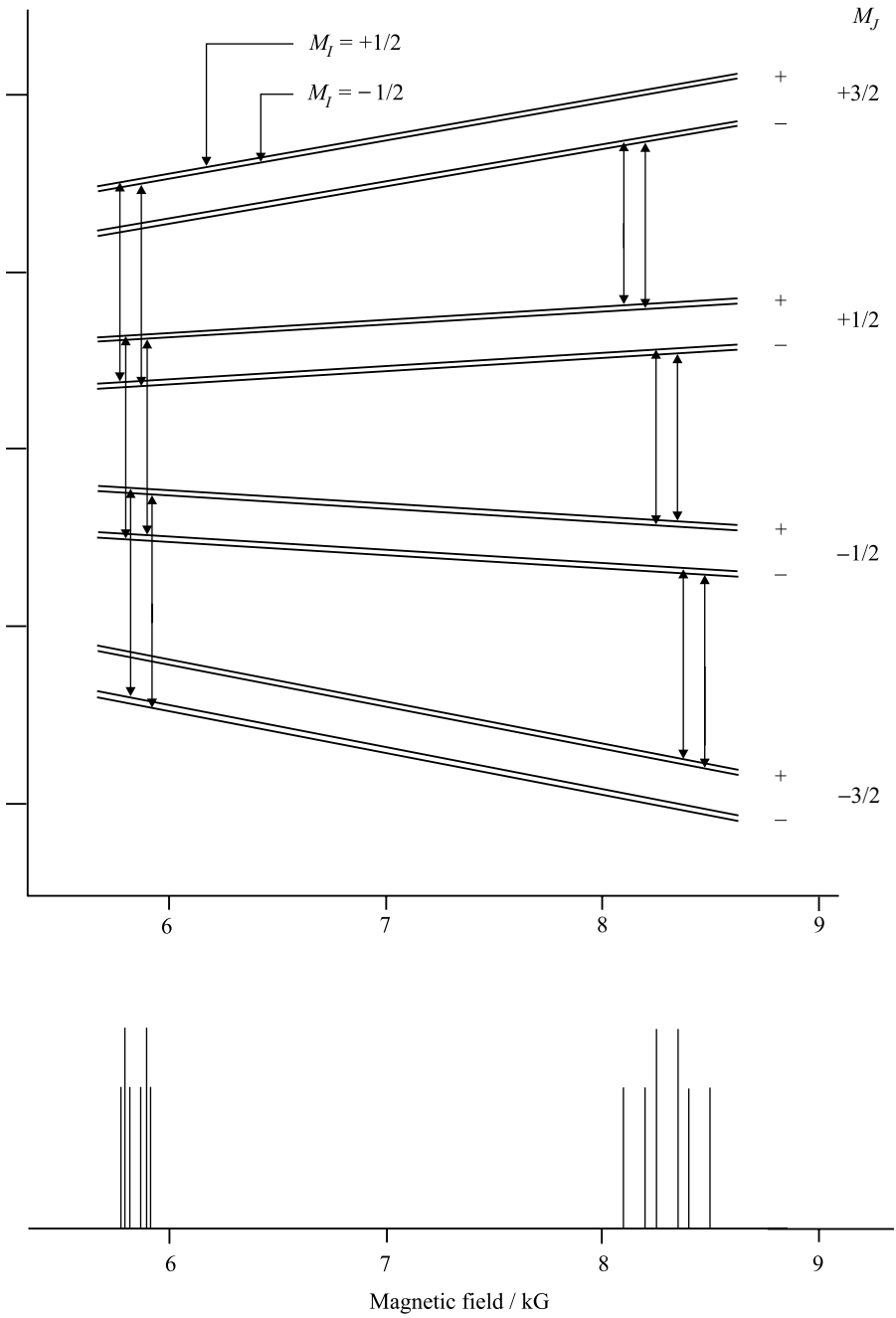

Figure 9.14. *Upper*: Zeeman behaviour of the Λ-doublet and proton hyperfine levels of OH in the $J = 3/2$ $F_1(^2\Pi_{3/2})$ rotational level, and the electric dipole transitions. *Lower*: stick diagram of the magnetic resonance spectrum obtained by Radford at a frequency of 9263 MHz [7].

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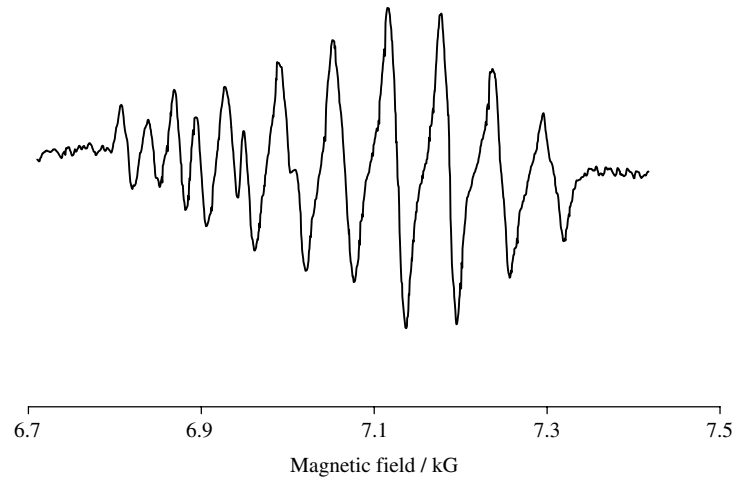

Figure 9.15. Microwave Λ-doublet magnetic resonance spectrum of OH in the $J = 9/2$ F_1 ($^2\Pi_{3/2}$) rotational level [66]. The resonant microwave frequency was 26254 MHz. Eighteen transitions are expected but only 13 lines are resolved.

spectrum obtained by Brown, Kaise, Kerr and Milton [66] arising from the $J = 9/2$ F_1 ($^2\Pi_{3/2}$) level. Radford realised that, because of the intermediate coupling behaviour in OH, the levels of the $^2\Pi_{1/2}$ component also show strong magnetic effects. He then went on to detect the microwave magnetic resonance spectrum of OH in the $J = 3/2$ and 5/3 levels of this upper component (F_2); his experimental spectrum for $J = 3/2$ is shown in figure 9.16. The six lines labelled in figure 9.16 arise from the following transitions.

$$\begin{aligned}
&f_1: \quad M_J = -3/2, \quad M_I = -1/2\,(+\text{parity}) \leftrightarrow M_J = -1/2, \quad M_I = -1/2\,(-\text{parity})\\
&f_2: \quad M_J = -1/2, \quad M_I = -1/2\,(+\text{parity}) \leftrightarrow M_J = +1/2, \quad M_I = -1/2\,(-\text{parity})\\
&f_3: \quad M_J = +1/2, \quad M_I = +1/2\,(+\text{parity}) \leftrightarrow M_J = +3/2, \quad M_I = +1/2\,(-\text{parity})\\
&f_4: \quad M_J = -1/2, \quad M_I = +1/2\,(+\text{parity}) \leftrightarrow M_J = +1/2, \quad M_I = +1/2\,(-\text{parity})\\
&f_5: \quad M_J = +1/2, \quad M_I = -1/2\,(+\text{parity}) \leftrightarrow M_J = +3/2, \quad M_I = -1/2\,(-\text{parity})\\
&f_6: \quad M_J = -3/2, \quad M_I = +1/2\,(+\text{parity}) \leftrightarrow M_J = -1/2, \quad M_I = +1/2\,(-\text{parity})
\end{aligned}$$

Radford's analysis of the magnetic resonance spectrum was ground-breaking by his extension of the theory of the Zeeman effect to the general intermediate coupling case. In addition to Radford's observations, Brown, Kaise, Kerr and Milton [66] recorded microwave magnetic resonance spectra at higher resonant frequencies and were able to observe, as we have seen, the $J = 9/2$ and also the $J = 11/2$ levels in the F_1 ($^2\Pi_{3/2}$) spin component. The frequencies of the zero magnetic field transitions involved in the microwave magnetic resonance studies had all been measured previously and much more accurately in molecular beam work by Meerts [38], as we described in chapter 8. Brown, Kaise, Kerr and Milton [66] therefore used the magnetic resonance measurements to provide a full determination of the magnetic properties of the OH radical. In their paper they gave the complete Zeeman Hamiltonian for a molecule

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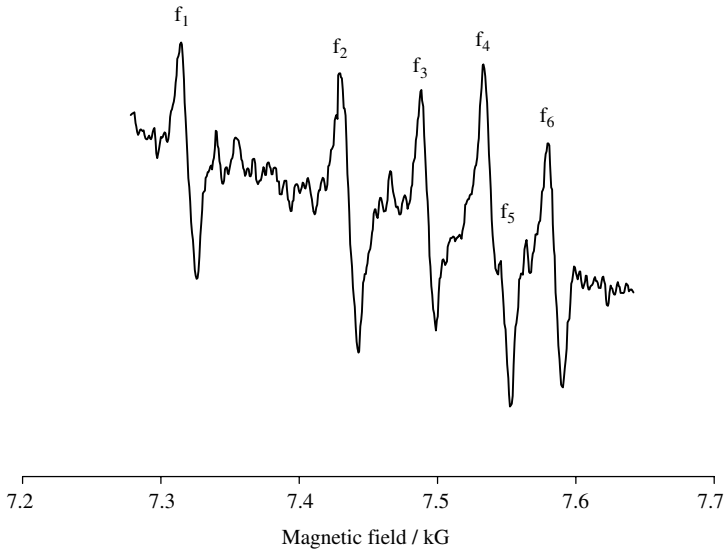

Figure 9.16. Recording of the Λ-doublet microwave magnetic resonance spectrum of OH in the $J = 3/2$ $F_2(^2\Pi_{1/2})$ rotational level [7]. The assignment of the lines is given in the text. The resonant microwave frequency was 9200 MHz.

in a $^{2S+1}\Pi$ electronic state and showed that it involves six determinable parameters (g-factors) in addition to the nuclear spin g-factor for the proton. Carrington and Lucas [39], in earlier work, extended our knowledge of the OH radical by studying ^{17}OH and determing the ^{17}O magnetic and electric hyperfine constants.

(iii) THEORY OF THE Λ-DOUBLING

As we discussed earlier in chapter 8, the Λ-doubling in a molecule such as OH arises from the $\Delta\Lambda = \pm 1$ terms in the spin–orbit and rotational Hamiltonians which mix the $^2\Pi$ ground state with excited $^2\Sigma$ states. These terms also mix the $^2\Pi$ state, $\Lambda = \pm 1$, with $^2\Delta$ states, for which $\Lambda = \pm 2$, but such mixing does not contribute to the Λ-doubling. In the case of OH, like LiO, the situation is particularly simple because the mixing is predominantly with a single excited state, the $A\,^2\Sigma^+$ state, which lies some 32 680 cm^{-1} above the ground state. It is therefore possible to analyse the observed Λ-doublet splittings explicitly in terms of the $X\,^2\Pi$ and $A\,^2\Sigma^+$ states. However, in general there will be varying contributions to the Λ-doubling from a host of $^2\Sigma$ states, both $^2\Sigma^+$ and $^2\Sigma^-$ in character. In order to cope with such a situation, the effects of the terms in the full Hamiltonian which are off-diagonal in the quantum number Λ are described by perturbation theory to produce an effective Hamiltonain. This effective Hamiltonian operates only within the manifold of levels of a particular electronic state, in this case the ground $^2\Pi$ state, but still reproduces the molecular eigenstates to the required accuracy. In principle, this procedure can be carried on indefinitely to any order of perturbation theory, as we showed in chapter 7. In practice, it becomes very hard work beyond third order.

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The effects of the off-diagonal terms when folded-in by perturbation theory are of two types. They can either produce operators of the same form as those which already exist in the Hamiltonian constructed from the $\Delta\Lambda = 0$ matrix elements (the zeroth-order Hamiltonian), or they can have a completely novel form. A good example of the former type is the second-order contribution to the rotational constant which arises from admixture of excited Σ and Δ states,

$$B = B^{(1)} + B^{(2)}. \tag{9.63}$$

The first-order part describes the nuclear and the second-order the electronic contribution to the molecular moment of inertia. The Λ-doubling terms, on the other hand, have no counterpart in the zeroth-order Hamiltonian. For a $^2\Pi$ state, the operator form is

$$\mathcal{H}_{\rm LD} = -(1/2)q(J_+^2 e^{-2i\phi} + J_-^2 e^{2i\phi}) + (1/2)(p+2q)(J_+ S_+ e^{-2i\phi} + J_- S_- e^{2i\phi}), \tag{9.64}$$

where p and q are the Λ-doubling parameters. (For a Π state of triplet or higher multiplicity, there is a third parameter, o. However, the terms which involve this parameter have no effect on $^2\Pi$ or $^1\Pi$ states.) The operators $J_\pm$are shift operators which act on the rotational basis functions with the selection rules $\Delta\Omega = \mp 1$, and $S_\pm$ are the corresponding operators which act on the spin basis functions with $\Delta\Sigma = \pm 1$ selection rules. In addition, the coordinate ϕ in equation (9.64) represents an electronic azimuthal angle, associated with the orbital angular momentum about the z axis. The exponential terms which involve ϕ ensure that $\mathcal{H}_{\rm LD}$ only has matrix elements which connect states whose Λ values differ by ± 2. Since a Π electronic state can be represented by a pair of basis functions $|\Lambda = +1\rangle$ and $|\Lambda = -1\rangle$, which are linked directly by $\mathcal{H}_{\rm LD}$, we see that the operator has a first-order effect for a $^{2S+1}\Pi$ electronic state. The full form of the effective Hamiltonian for Λ-doubling was first given by Brown, Kopp, Malmberg and Rydh [63] although the seeds of the idea were sown in just about the very first treatment of this topic, by Mulliken and Christy [40] in 1931.

The Λ-doubling operator can be written in spherical tensor notation:

$$\mathcal{H}_{\rm LD} = \sum_{q=\pm 1} \exp(-2iq\phi)\left\{-q\mathrm{T}^2_{2q}(\boldsymbol{J}, \boldsymbol{J}) + (p+2q)\mathrm{T}^2_{2q}(\boldsymbol{J}, \boldsymbol{S})\right\}. \tag{9.65}$$

In a Hund's case (a) basis set the matrix elements of (9.65) are as follows:

$$\begin{aligned}
&\langle \eta, \Lambda; S, \Sigma; J, \Omega, M_J | \mathcal{H}_{\rm LD} | \eta, \Lambda'; S, \Sigma'; J, \Omega', M_J \rangle \\
&\quad = \sum_{q=\pm 1} \delta_{\Lambda', \Lambda \mp 2} \left\{ \delta_{\Sigma,\Sigma'} (1/2\sqrt{6}) q (-1)^{J-\Omega} \begin{pmatrix} J & 2 & J \\ -\Omega & -2q & \Omega' \end{pmatrix} [(2J-1)(2J) \right. \\
&\qquad \times (2J+1)(2J+2)(2J+3)]^{1/2} + (p+2q)(-1)^{J-\Omega+S-\Sigma} \begin{pmatrix} J & 1 & J \\ -\Omega & -q & \Omega' \end{pmatrix} \\
&\qquad \left. \times \begin{pmatrix} S & 1 & S \\ -\Sigma & q & \Sigma' \end{pmatrix} [J(J+1)(2J+1)S(S+1)(2S+1)]^{1/2} \right\}.
\end{aligned} \tag{9.66}$$

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We have used the result

$$\langle \Lambda = \pm 1 | \exp(\pm 2i\phi) | \Lambda = \mp 1 \rangle = -1, \tag{9.67}$$

which implies a particular phase choice for the orbital function [66]. The role which these terms play in the matrix and their ultimate contribution to the energy levels can best be appreciated by re-casting the matrix elements in parity-conserving combinations of case (a) functions,

$$\begin{aligned} &|\Lambda; J, |\Omega|; \pm\rangle \\ &\quad = \frac{1}{\sqrt{2}}\{|\Lambda = 1; S, \Sigma; J, \Omega, M_J\rangle \pm (-1)^{J-S}|\Lambda = -1; S, -\Sigma; J, -\Omega, M_J\rangle\}. \end{aligned} \tag{9.68}$$

With appropriately chosen basis functions [66], the upper sign choice is a function with positive parity and the lower sign choice has negative parity. In this basis, the matrix elements of $\mathcal{H}_{\rm LD}$ are:

$$\begin{aligned} &\langle \Lambda; J, |\Omega|; \pm | \mathcal{H}_{\rm LD} | \Lambda; J, |\Omega'|; \pm\rangle \\ &\quad = \pm(-1)^{J-S}\left\{\delta_{\Sigma,\Sigma'}(1/2\sqrt{6})q(-1)^{J+\Omega}\begin{pmatrix} J & 2 & J \\ \Omega & -2 & \Omega' \end{pmatrix}[(2J-1)(2J)(2J+1)\right. \\ &\qquad \times (2J+2)(2J+3)]^{1/2} + (p+2q)(-1)^{J+\Omega+S+\Sigma}\begin{pmatrix} J & 1 & J \\ \Omega & -1 & \Omega' \end{pmatrix}\begin{pmatrix} S & 1 & S \\ \Sigma & 1 & \Sigma' \end{pmatrix} \\ &\qquad \left. \times [J(J+1)(2J+1)S(S+1)(2S+1)]^{1/2}\right\}. \end{aligned} \tag{9.69}$$

These matrix elements contribute with one sign for the positive parity matrix and with the opposite sign for the negative parity matrix. Note that, because $\mathcal{H}_{\rm LD}$ commutes with the laboratory-fixed inversion operator E*, which defines parity, matrix elements between states of opposite parity are rigorously zero.

The matrix representation of the Λ-doubling terms for a molecule in a $^2\Pi$ state has been given in chapter 8. For completeness and continuity, we repeat it here. There is a 2×2 matrix for the states with a given J value, as follows.

	$^2\Pi_{3/2}$	$^2\Pi_{1/2}$
$^2\Pi_{3/2}$	0	$\pm(-1)^{J-1/2}(q/2)(J+1/2)[(J+1/2)^2-1]^{1/2}$
$^2\Pi_{1/2}$	$\pm(-1)^{J-1/2}(q/2)(J+1/2)$ $\times[(J+1/2)^2-1]^{1/2}$	$\mp(-1)^{J-1/2}(1/2)(p+2q)(J+1/2)$

The upper and lower signs refer to states of positive and negative parity respectively.

As mentioned above, the small mass of OH leads to a pronounced centrifugal distortion of its rotational and spin energy levels. The description of these effects has already been given earlier in section 8.5.4(*d*), where the explicit matrix elements for a molecule in a $^2\Pi$ state were given.

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(iv) ZEEMAN EFFECT

Perhaps the most important interaction in the microwave magnetic resonance experiment is that between the molecular magnetic dipole moment and the applied magnetic field, represented by the Zeeman Hamiltonian. We have already introduced this operator in our discussion of the spectra of ClO and BrO, equation (9.37). However, this form is tailored to the description of the energy levels of a molecule in a $^2\Pi_{3/2}$ spin component which shows good case (a) behaviour and a negligible Λ-doubling. For a more complicated situation, such as that for OH, other terms have to be added to this operator. We now give the complete form for the Zeeman Hamiltonian, foreshadowed by the work of Radford [7] and put into effective operator form by Brown and Uehara [10] and by Brown, Kaise, Kerr and Milton [66], as follows:

$$\begin{aligned}
\mathcal{H}_Z = {} & g'_L \mu_B B_Z \mathrm{T}^1_{p=0}(\boldsymbol{L}) && \text{(i)}\\
& + g_S \mu_B B_Z \mathrm{T}^1_{p=0}(\boldsymbol{S}) && \text{(ii)}\\
& - g_r \mu_B B_Z \mathrm{T}^1_{p=0}(\boldsymbol{J}-\boldsymbol{L}-\boldsymbol{S}) && \text{(iii)}\\
& + g_l \mu_B B_Z \sum_{q=\pm 1} \mathfrak{D}^{(1)}_{0q}(\omega)^* \, \mathrm{T}^1_q(\boldsymbol{S}) && \text{(iv)}\\
& - g_N \mu_N B_Z \mathrm{T}^1_{p=0}(\boldsymbol{I}) && \text{(v)}\\
& + g'_l \mu_B B_Z \sum_{q=\pm 1} \exp(-2\mathrm{i}q\phi)\mathfrak{D}^{(1)}_{0,-q}(\omega)^* \mathrm{T}^1_q(\boldsymbol{S}) && \text{(vi)}\\
& - g_r^{e'} \mu_B B_Z \sum_{q=\pm 1} \sum_p \exp(-2\mathrm{i}q\phi)(-1)^p \mathfrak{D}^{(1)}_{-p,-q}(\omega)^* \mathrm{T}^1_p(\boldsymbol{J}-\boldsymbol{S})\mathfrak{D}^{(1)}_{0,-q}(\omega)^*. && \text{(vii)}
\end{aligned} \tag{9.70}$$

The seven terms in this expression represent the following interactions:

(i) the orbital Zeeman effect. The orbital g-factor, g'_L, is so called (rather than simply g_L) because it contains relativistic, diamagnetic and non-adiabatic contributions;
(ii) the electron spin isotropic contribution;
(iii) the rotational magnetic moment contribution to the Zeeman effect;
(iv) the anisotropic contribution to the electron spin Zeeman effect, which takes account of the cylindrical symmetry shown by a diatomic molecule;
(v) the nuclear spin Zeeman effect;
(vi) and (vii) are two terms which are parity-dependent and effectively mark the reduction of the electronic distribution from cylindrical to a lower symmetry.

There are seven g-factors in equation (9.70). The two major ones are g'_L and g_S which are expected to have values very near to 1.0 and 2.002. In a real molecule, however, the values will differ slightly but significantly from these values. In practice, their values are determined along with those of all the others from measurements of the molecule in a known magnetic field. Only the nuclear spin g factor, g_N, is effectively a known quantity. Its apparent value will be subject to chemical shifts in any given molecular environment, of course, but such effects are much too small to be observable in a gas phase magnetic resonance experiment. Ignoring the nuclear spin

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g-factor, therefore, we see that there are six determinable parameters, or g-factors, in equation (9.70) which are required to describe the Zeeman interaction for a molecule in a $^{2S+1}\Pi$ state fully.

The matrix elements of the Zeeman Hamiltonian given in equation (9.70) are evaluated most appropriately in an I-decoupled basis set because the nuclear spin is decoupled in almost all situations in quite modest magnetic fields. The matrix elements of the simpler Zeeman Hamiltonian have been given earlier in equations (9.56) to (9.60). For the sake of completeness, we give the matrix elements of the full Zeeman Hamiltonian here:

$$
\begin{aligned}
&\langle \Lambda; S, \Sigma; J, \Omega, M_J; I, M_I | \mathcal{H}_Z | \Lambda'; S, \Sigma'; J', \Omega', M_J; I, M_I \rangle \\
&= \mu_B B_Z \delta_{\Lambda,\Lambda'} \sum_q (-1)^{J-M_J+J-\Omega} [(2J+1)(2J'+1)]^{1/2} \begin{pmatrix} J & 1 & J' \\ -M_J & 0 & M_J \end{pmatrix} \\
&\quad \times \begin{pmatrix} J & 1 & J' \\ -\Omega_J & q & \Omega' \end{pmatrix} \Big\{ (g'_L + g_r) \Lambda \delta_{\Sigma,\Sigma'} + (g_S + g_r + g_l)(-1)^{S-\Sigma} \\
&\quad \times [S(S+1)(2S+1)]^{1/2} \begin{pmatrix} S & 1 & S \\ -\Sigma & q & \Sigma' \end{pmatrix} - g_l \Sigma \delta_{\Sigma,\Sigma'} \Big\} \\
&\quad - (g_r \mu_B B_Z M_J + g_N \mu_N B_Z M_I) \delta_{J,J'} \delta_{\Sigma,\Sigma'} \delta_{\Lambda,\Lambda'} \\
&\quad - \mu_B B_Z \sum_{q=\pm 1} \delta_{\Lambda,\Lambda\mp 2} (-1)^{J-M_J} [(2J+1)(2J'+1)]^{1/2} \begin{pmatrix} J & 1 & J' \\ -M_J & 0 & M_J \end{pmatrix} \\
&\quad \times \Big[\big(g'_l - g_r^{e'}\big)(-1)^{S-\Sigma} \begin{pmatrix} S & 1 & S \\ -\Sigma & q & \Sigma' \end{pmatrix} [S(S+1)(2S+1)]^{1/2} (-1)^{J-\Omega} \\
&\quad \times \begin{pmatrix} J & 1 & J' \\ -\Omega & -q & \Omega' \end{pmatrix} - g_r^{e'} \delta_{\Sigma,\Sigma'} (-1)^{J-\Omega} \sum_{\Omega''} (1/2) \Big\{ (-1)^{J-\Omega''} \begin{pmatrix} J & 1 & J \\ -\Omega & -q & \Omega'' \end{pmatrix} \\
&\quad \times \begin{pmatrix} J & 1 & J' \\ -\Omega'' & -q & \Omega' \end{pmatrix} [J(J+1)(2J+1)]^{1/2} + (-1)^{J'-\Omega''} \begin{pmatrix} J & 1 & J' \\ -\Omega & -q & \Omega'' \end{pmatrix} \\
&\quad \times \begin{pmatrix} J' & 1 & J' \\ -\Omega'' & -q & \Omega' \end{pmatrix} [J'(J'+1)(2J'+1)]^{1/2} \Big\} \Big]. \qquad (9.71)
\end{aligned}
$$

A complete determination of the Zeeman parameters for OH has been made by Brown, Kaise, Kerr and Milton [66]. They first re-fitted Meerts' data on the Λ-doubling frequencies [38] to provide accurate zero-field frequencies. They then combined their measurements with those made earlier by Radford [7] to determine the g-factors. The results of their fits are given in table 9.4. The values given in table 9.4 form a representative set and demonstrate some general points. First, the broad features of the Zeeman interaction are described by two major parameters, g'_L and g_S, which are typically three orders-of-magnitude larger than the other four g-factors. Second, these two parameters have values close to those expected for a free electron (1.0 and 2.002 respectively) so the Zeeman effect can be predicted quite reliably before any experimental observations are attempted. Finally, it can be seen that the two major g-factors differ significantly from the expected free electron values, and the other four parameters have significant non-zero values.

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Table 9.4. *g-Factors for OH in the $X\,^2\Pi$ state [66]. The calculations are made by assuming that the $X\,^2\Pi$ and $A\,^2\Sigma^+$ states are in pure precession*

Parameter	Experimental value	Calculated value
g'_L	1.001 07 (15)	1.000 93
g_S	2.001 52 (36)	2.002 06
$10^3\, g_l$	4.00 (56)	4.29
$10^3\, g_r$	−0.633 (19)	−0.55
$10^3\, g'_l$	6.386 (30)	8.58
$10^3\, g_r^{e'}$	2.0446 (23)	2.19

All of the experimentally determined quantities carry information on the electronic structure of the OH radical. A very simple picture of this structure which actually works very well is to describe the properties in terms of the wave functions for two electronic states only, the $X\,^2\Pi$ and $A\,^2\Sigma^+$ states, with electronic configurations

$$\cdots(2p\sigma)^2(2p\pi)^3 \quad X\,^2\Pi$$
$$\cdots(2p\sigma)^1(2p\pi)^4 \quad A\,^2\Sigma^+.$$

We can then make an even more drastic approximation and represent the molecular orbitals in these configurations by pure $2p$ atomic orbitals on the O atom. This approximation was called pure precession by Van Vleck [41]; in this approximation the electrons in these outermost orbitals are in a spherically symmetric environment and they have a well defined value of the orbital angular momentum quantum number l (unity for a p orbital). In the pure precession approximation, we can derive very simple expressions for the g-factors [66]. The values for OH predicted on the basis of this very simple model are given in table 9.4. The fact that they agree reasonably well with the experimental numbers suggests that the theoretical model is essentially correct.

(b) Far-infrared laser magnetic resonance spectrum of OH

The OH molecule was one of the first molecules to be studied by the fledgling technique of far-infrared laser magnetic resonance (FIR LMR) in the early 1970s [42]. At that stage there were very few FIR laser lines available; for all of them, the population inversion was created in the gain medium by electric discharge, through H_2O, D_2O or HCN vapour. It is a remarkable coincidence that many of the water discharge lines are very close in frequency to OH transitions in the $v = 0$ level, particularly when one considers that OH is a light molecule with a very open rotational spectrum. It was for this reason that the water discharge laser was familiarly referred to as the 'OH laser' by workers in the field. The various FIR LMR studies of OH in the $v = 0$ level of its $X\,^2\Pi$ state were collected together in a paper by Brown, Kerr, Wayne, Evenson and Radford [43]. The energy level diagram for OH in this state, showing the transitions studied, has already been illustrated in figure 9.13. Of the seven laser lines used in this

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study, five are lines from the water discharge laser. The transitions are of two types: pure rotational transitions within a given spin component, and fine-structure transitions between the two spin components. The latter are usually weaker than the former; they are actually electric dipole forbidden in the case (a) limit.

The dominant source of line broadening in a spectral transition in the far-infrared is the Doppler effect. For a light molecule such as OH at room temperature, the Doppler linewidth at 100 cm^{-1} (corresponding to a wavelength of 100 μm) is 0.000 30 cm^{-1} or 9.0 MHz. This is comparable with, and sometimes larger than, the proton hyperfine splittings in OH. For this reason, the proton hyperfine splittings cannot always be observed on resonances in the LMR spectrum. In such a situation, the intra-cavity aspect of the FIR LMR apparatus comes into its own because it provides a natural environment to produce saturation or Lamb dips on the absorption signals. Lamb dips arise when radiation of a given frequency passes through the same region of the molecular sample simultaneously from opposite directions. The linewidth of a Lamb dip is usually dictated by lifetime limiting effects of the levels involved; in the case of OH this is pressure broadening. The increase in resolution obtainable with Lamb dips is demonstrated in figure 9.17, which shows part of the LMR spectrum of OH recorded with the 84.3 μm line of the water discharge laser. The broader background is the residual Doppler profile (or rather, its first derivative) on which are superimposed the two Lamb dips; these correspond to the proton hyperfine doublet, also as first derivatives, but with opposite phases.

Measurements of the FIR LMR spectrum of OH are less accurate than those of the field-free Λ-doubling spectrum in the microwave region, partly because they are made at much higher frequencies (with correspondingly larger linewidths), and partly

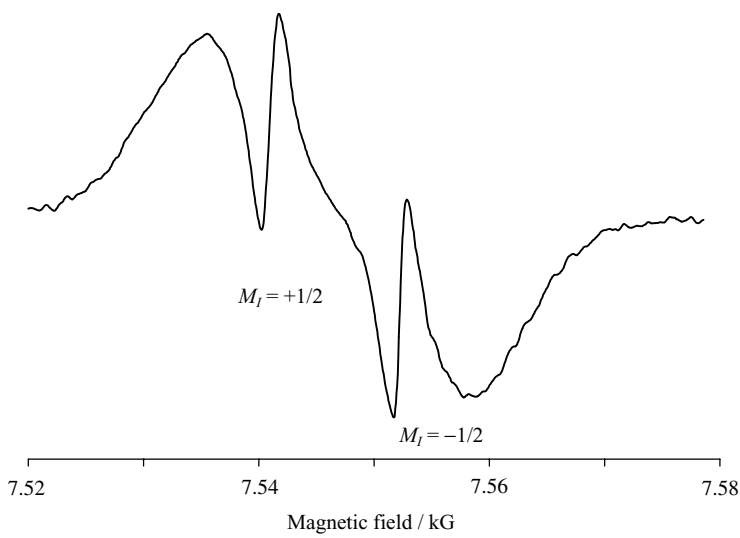

Figure 9.17. A line in the 84 μm LMR spectrum of OH; this line is one Zeeman component of the $J = 7/2 \leftrightarrow 5/2$ $F_1(^2\Pi_{3/2})$ rotational transition. The Lamb dips correspond to the proton hyperfine splitting which is otherwise hidden in the overall Doppler profile [43].

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because they involve magnetic field rather than frequency measurements. Brown, Kerr, Wayne, Evenson and Radford [43] therefore used the data from the FIR LMR spectrum to determine the values of the major parameters A_0, γ_0, B_0 and D_0, constraining the Λ-doubling, hyperfine and Zeeman parameters to the values obtained by earlier workers. The values obtained were a considerable improvement on the best available at the time which had been determined from the $A\,^2\Sigma^+$–$X\,^2\Pi$ electronic transition in the ultraviolet region. Since then they have been superseded by observations of the rotational and fine structure spectrum of OH by field-free tunable FIR techniques [44], which are described in detail in chapter 10.

The dominant isotopic form of the radical is, of course, $^{16}O^1H$. Following its study by FIR LMR, observations were also made of the spectra of other less-abundant isotopomers, including $^{16}O^2D$ [45] and $^{18}O^1H$ [46] in natural abundance, and artificially enriched $^{17}O^1H$ [47]. Much of the motivation for these studies was the detection of OH in remote regions such as the interstellar gas clouds, or the middle regions of the earth's atmosphere.

9.4.4. Far-infrared laser magnetic resonance of CH in the $X\,^2\Pi$ ground state

(a) Introduction

The CH radical is an important molecule in both chemistry and physics. It has long been familiar to optical astronomers through its interstellar absorption spectrum. The fact that the spectrum is so simple, consisting of a single line, the $R_2(1)$ line in the $A\,^2\Delta$–$X\,^2\Pi$ transition, was the first indication that not only do the interstellar gas clouds contain molecular species but also that their temperature is very low. Apart from its astronomical significance, the CH radical is an enthusiastic participant in most combustion processes. A proper knowledge of the way in which it is involved requires a full determination of its physical properties and the development of experimental methods for its detection at low concentrations. These objectives have fuelled a large amount of research on the spectroscopy of CH, not all of it successful. It was one of the early triumphs of FIR LMR to provide a laboratory detection of a rotational transition in CH [48]; this followed several unsuccessful attempts to detect its microwave Λ-doubling spectrum by either magnetic resonance or field-free techniques. Equally, it was a major coup for the radioastronomers to be able to detect and measure the 3.3 GHz Λ-doubling transition in the interstellar medium [49, 50], long before detection in the laboratory. Such has been the progress made in subsequent years that laboratory studies of CH are now almost routine.

(b) Hund's case (b) behaviour in $^2\Pi$ states

From a spectroscopic point of view, CH is quite similar to OH. It has a $^2\Pi$ ground state and a large rotational constant. In consequence, Λ-doubling and centrifugal distortion

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